Second Anisotropy Constant in Cubic Ferromagnetic Crystals*†

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The second anisotropy constant, K_2, is evaluated at $0°K$ for cubic, ferromagnetic crystals using two-particle dipole- and quadrupole-like interactions as perturbations on a molecular field Hamiltonian. In second- and third-order perturbation, the energy denominators are modified to take into account the effect on the molecular field of the exchange interaction of consecutively reversed spins. The expression for $K_2(0)$ is used in conjunction with that for $K_1(0)$ to calculate the values of the pseudodipolar and pseudoquadrupolar coupling constants for iron, cobalt, and nickel. For bcc Fe, $D/J = 0.0793$ and $Q/J = 0.00157$, where $JS = 2.87 \times 10^{-14}$ erg; for fcc Co, $D/J = 0.113$ and $Q/J = 0.000865$, where $JS = 2.0 \times 10^{-14}$ erg; and for fcc Ni, $D/J = -0.0768$ and $Q = 0$, where $JS = 2.5 \times 10^{-14}$ erg, although the application of the model to nickel is not entirely satisfactory. These values are used to predict the size of the third anisotropy constant and the paramagnetic resonance linewidth.

I. INTRODUCTION

PART of the free energy of ferromagnetic crystals is dependent on the direction of the magnetization vector relative to the crystal axes, i.e., is anisotropic. In crystals with cubic symmetry, the deviation from complete isotropy is at least quartic in the direction cosines of the magnetization vector taken with respect to the cubic axes. This anisotropy energy is usually written as

$$F_A(T) = K_1(T)(\alpha_1^2\alpha_2^2 + \alpha_1^2\alpha_3^2 + \alpha_2^2\alpha_3^2)$$
$$+ K_2(T)\alpha_1^2\alpha_2^2\alpha_3^2 + \cdots, \quad (1)$$

or

$$F_A'(T) = \kappa_4(T)\Gamma_4(\alpha_1,\alpha_2,\alpha_3) + \kappa_6(T)\Gamma_6(\alpha_1,\alpha_2,\alpha_3) + \cdots, \quad (2)$$

where F_A and F_A' differ only by the inclusion of some isotropic terms in the latter. The K's are known as anisotropy constants and the κ's as anisotropy coefficients.[1,2] In Eq. (2) the angular functions are unnormalized surface harmonics having cubic symmetry:

$$\Gamma_4 \equiv \alpha_1^2\alpha_2^2 + \alpha_1^2\alpha_3^2 + \alpha_2^3\alpha_3^2 - 1/5, \quad (3)$$

$$\Gamma_6 \equiv \alpha_1^2\alpha_2^2\alpha_3^2 - (1/11)(\alpha_1^2\alpha_2^2 + \alpha_1^2\alpha_3^2 + \alpha_2^2\alpha_3^2) + 2/231. \quad (4)$$

Neglecting surface harmonics beyond the sixth, the K's and κ's are related by

$$\kappa_4 = K_1 + (1/11)K_2; \quad \kappa_6 = K_2. \quad (5)$$

Classical, macroscopic considerations[1] give the temperature dependence of the anisotropy coefficients as

$$\kappa_n(T)/\kappa_n(0) = [M(T)/M(0)]^{n(n+1)/2}, \quad (6)$$

where $M(T)$ is the spontaneous magnetization and n is the order of the surface harmonic. In particular, κ_4 (and thus K_1 if $K_1 \gg K_2$) is predicted to follow a "10th power law," and κ_6 (or K_2) a "21st power law." Microscopic calculations of K_1, using molecular field theory[3] and the method of spin waves,[4] have been shown to agree with the 10th power law; no similar calculations have provided an explicit temperature dependence for K_2.

The statistical fluctuations underlying Eq. (6) always lead to a 10th power law for K_1, at least at low temperatures, if the local anisotropy or atomic coupling constants are assumed independent of temperature. Since the magnetocrystalline anisotropy of iron and nickel as determined experimentally shows wide variation from the statistical 10th power law, there have been many attempts either to redetermine $K_1(T)$ from first principles or to derive a modifying temperature-dependent factor, $k_{\text{local}}(T)$.

Among the former type are the calculations of Brooks[5] and Fletcher[6] using the collective electron model. Both authors conclude, however, that their functional temperature dependence is far too weak to explain the rapid decrease with increasing temperature of K_1 in Ni, which falls off approximately as the 50th power of $M(T)$. Merkle[7] has calculated a local anisotropy factor for nickel which is proportional to T^2, but the over-all agreement of his $K_1(T)$ with experiment is still poor. Recently, Slonczewski[8] pointed out that a term representing the changes in occupation of states caused by spin-orbit perturbation was neglected in these band theory calculations.[5-7] The neglected term has a cancelling effect such that the magnitude of the calculated anisotropy is greatly reduced. What

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[5] H. Brooks, Phys. Rev. 58, 909 (1940).
[6] G. C. Fletcher, Proc. Phys. Soc. (London) A67, 505 (1954); 78, 145 (1961).
[7] K. Merkle, Z. Naturforsch. 14a, 938 (1959).
[8] J. C. Slonczewski, Suppl. J. Phys. Soc. Japan B-I, 17, 34 (1962).

effect this cancellation has on the temperature dependence of the anisotropy was not determined.

Again for Ni and also for Fe, where $K_1(T) \propto M(T)^4$ at low temperatures,[9] Brenner,[10] and Carr[11] have proposed a strain-dependent k_{local} proportional to T. However, Kouvel and Wilson[12] have demonstrated that this term cannot modify the 10th power law sufficiently to provide agreement with experimental data. The anisotropy constants of face-centered cubic cobalt appear to follow the statistical laws with only a slight modification for thermal expansion.[13] In general, however, the temperature dependence of ferromagnetic anisotropy is not well understood. The present paper is concerned only with $K(0)$ which is a measure of the intrinsic anisotropic coupling between magnetic atoms.

Van Vleck's molecular field theory of ferromagnetic anisotropy[3] is the basis of this investigation. In his theory Van Vleck reasoned that, since single-ion anisotropy in cubic crystals only exists for $S \geq 2$ (2^4 pole), the origin of anisotropy in cubic crystals of lower atomic spin would probably be in two-particle interactions. Further, the magnetic dipole interaction being too small to account for the observed magnitude of F_A, he introduced the pseudodipolar and pseudoquadrupolar interactions. These interactions have exactly the same form as the usual multipole interactions, but have a much larger constant of proportionality:

$$\mathcal{H}_D = \sum_{i>j} D_{ij}[\mathbf{S}_i \cdot \mathbf{S}_j - 3r_{ij}^{-2}(\mathbf{S}_i \cdot \mathbf{r}_{ij})(\mathbf{S}_j \cdot \mathbf{r}_{ij})], \quad (7)$$

$$\mathcal{H}_Q = \sum_{i>j} Q_{ij} r_{ij}^{-4} (\mathbf{S}_i \cdot \mathbf{r}_{ij})^2 (\mathbf{S}_j \cdot \mathbf{r}_{ij})^2. \quad (8)$$

Despite their simple form, $\mathcal{H}_D$ and $\mathcal{H}_Q$ actually arise from coupling between spin-orbit and orbit-crystalline field interactions. Since $\mathcal{H}_D$ is only quadratic in the direction cosines, it cannot contribute to $K_1(0)$ in first order, i.e., in a classical sense. Similarly $\mathcal{H}_Q$ cannot contribute to $K_2(0)$ in a classical sense. By carrying the calculation through the third order of perturbation, an expression for $K_2(0)$ is derived which, in conjunction with the expression for $K_1(0)$, determines the values of the phenomenological atomic coupling constants, D and Q.

The Hamiltonians (7) and (8) are discussed further in Sec. II and are evaluated as perturbations on the energy levels of the unperturbed Hamiltonian,

$$\mathcal{H}_0 = g\mu_B(H_E + H_0)\sum_i S_i^z, \quad (9)$$

where H_E is the Weiss molecular field and H_0 is the applied field. In Eq. (9), μ_B is positive and the z axis is in the direction of H_0. One of the principal approximations of the Van Vleck theory is the replacement of

an isotropic exchange Hamiltonian by a molecular field Hamiltonian. However, the methods of molecular field theory and spin wave theory (neglecting exchange interaction of spin waves) have been shown[4] to give equivalent results when the spin wave energy denominators of second and higher order perturbation terms are assumed independent of $\mathbf{k}$, and the calculations of Charap and Weiss have shown this constant denominator approximation to be quite good [see Eq. (26)].

The expression for the first anisotropy constant, $K_1(0)$, is given in Sec. III, and that for the second anisotropy constant, $K_2(0)$, in Sec. IV. Using measured values of K_1, K_2, and J, this pair of equations can be solved for the values of the pseudodipolar and pseudoquadrupolar coupling constants, D and Q. This is done for cubic iron, cobalt, and nickel in Sec. V.

II. FREE ENERGY AND PERTURBING HAMILTONIAN

The free energy, F, is given by

$$\exp(-\beta F) = \mathrm{Tr}[\exp(-\beta \mathcal{H})], \quad (10)$$

where $\exp(-\beta \mathcal{H})$ is sometimes called the density operator, and

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' = \mathcal{H}_0 + \mathcal{H}_D + \mathcal{H}_Q. \quad (11)$$

For low temperatures a perturbative expansion in integral form[14] of the right-hand side of Eq. (10) yields an explicit expression for the nth-order contribution of $\mathcal{H}'$ to the free energy. For example, the second-order contribution is

$$F^{(2)} = \frac{1}{2}\left\{ \beta[F^{(1)}]^2 - Z_0^{-1}\sum_{n,m}|\mathcal{H}_{mn}'|^2\left(\frac{e^{-\beta E_m} - e^{-\beta E_n}}{E_n - E_m}\right)\right\}, \quad (12)$$

where

$$F^{(1)} = Z_0^{-1}\sum_n \mathcal{H}_{nn}' e^{-\beta E_n}; \quad Z_0 = \sum_n e^{-\beta E_n}. \quad (13)$$

Here one sees explicitly that if the system is degenerate, i.e., if $E_m = E_n$ for $m \neq n$, the vanishing energy denominators are cancelled exactly by the vanishing Boltzmann factors in the numerators. In the limit of $\beta \to \infty$, it can be shown that

$$F(0) = E_g + \mathcal{H}_{gg}' + \sum_m{}' \frac{|\mathcal{H}_{mg}'|^2}{E_g - E_m} + \sum_l{}'\sum_m{}' \frac{\mathcal{H}_{gm}' \mathcal{H}_{ml}' \mathcal{H}_{lg}'}{(E_g - E_m)(E_g - E_l)} - \mathcal{H}_{gg}'\sum_m{}' \frac{|\mathcal{H}_{mg}'|^2}{(E_g - E_m)^2}, \quad (14)$$

where E_g is the ground-state eigenvalue of Eq. (9) and the prime on the summation sign indicates omission of the term for which the summation index equals g. Equation (14) is formally equivalent to the standard

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[10] R. Brenner, Phys. Rev. 107, 1539 (1957).
[11] W. J. Carr, Jr., Phys. Rev. 109, 1971 (1958); J. Appl. Phys. 31, 69 (1960).
[12] J. S. Kouvel and R. H. Wilson, Suppl. J. Appl. Phys. 32, 276 (1961).
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[14] M. L. Goldberger and E. N. Adams, II, J. Chem. Phys. 20, 240 (1952); S. Nakajima, Suppl. Phil. Mag. 4, 363 (1955); M. Dresden, Rev. Mod. Phys. 33, 265 (1961).

result through third order of nondegenerate perturbation theory in quantum mechanics.

The perturbing Hamiltonian is rewritten in terms of the spin raising and lowering operators, $S^{\pm}$, using the very convenient notation introduced by Cooper and Keffer.[15] These authors defined the following symbols:

$$i^{\pm} \equiv \tfrac{1}{2}S_i^{\pm}; \quad i^z \equiv S_i^z; \quad i^{zz} \equiv i^z i^z;$$

$$i^{\pm\pm} \equiv i^{\pm}i^{\pm}; \quad i^{\pm z} \equiv \tfrac{1}{2}(i^{\pm}i^z + i^z i^{\pm});$$

$$i^{00} \equiv i^{zz} - i^+ i^- - i^- i^+ = \tfrac{3}{2}(S_i^z)^2 - \tfrac{1}{2}(\mathbf{S}_i)^2; \quad (15)$$

$$(ij)^{00} \equiv \tfrac{3}{2}S_i^z S_j^z - \tfrac{1}{2}\mathbf{S}_i \cdot \mathbf{S}_j;$$

$$m_{ij} = -m_{ji} \equiv \alpha_{ij} - i\beta_{ij}; \quad p_{ij} \equiv -p_{ji} \equiv \alpha_{ij} + i\beta_{ij}.$$

In the last pair of equations α_{ij}, β_{ij}, and γ_{ij} are the direction cosines of $\mathbf{r}_{ij}$ with respect to the axes of quantization. An example of the use of these symbols is

$$r_{ij}^{-1}\mathbf{S}_i \cdot \mathbf{r}_{ij} = i^+ m_{ij} + i^- p_{ij} + i^z \gamma_{ij}.$$

The expansion of the dipolar Hamiltonian is

$$\mathcal{H}_D = \mathcal{H}_D{}^2 + \mathcal{H}_D{}^1 + \mathcal{H}_D{}^0, \quad (16)$$

where

$$\mathcal{H}_D{}^2 \equiv -\tfrac{3}{2}\sum_{i \neq j} D_{ij} i^+ j^+ m_{ij}{}^2 + \text{c.c.},$$

$$\mathcal{H}_D{}^1 \equiv -3\sum_{i \neq j} D_{ij} i^+ j^z m_{ij}\gamma_{ij} + \text{c.c.}, \quad (17)$$

$$\mathcal{H}_D{}^0 \equiv \tfrac{1}{2}\sum_{i \neq j} D_{ij}(ij)^{00}(1 - 3\gamma_{ij}{}^2),$$

and c.c. means complex conjugate. Similarly the expansion of the quadrupolar Hamiltonian is

$$\mathcal{H}_Q = \mathcal{H}_Q{}^4 + \mathcal{H}_Q{}^3 + \mathcal{H}_Q{}^2 + \mathcal{H}_Q{}^1 + \mathcal{H}_Q{}^0, \quad (18)$$

where

$$\mathcal{H}_Q{}^4 \equiv \tfrac{1}{2}\sum_{i \neq j} Q_{ij} i^{++} j^{++} m_{ij}{}^4 + \text{c.c.},$$

$$\mathcal{H}_Q{}^3 \equiv 2\sum_{i \neq j} Q_{ij} i^{++} j^{+z} m_{ij}{}^3 \gamma_{ij} + \text{c.c.},$$

$$\mathcal{H}_Q{}^2 \equiv \sum_{i \neq j} Q_{ij}\{i^{++}[j^{zz} - j^{00}(1 - \gamma_{ij}{}^2)]$$
$$+ 2i^{+z}j^{+z}\gamma_{ij}{}^2\}m_{ij}{}^2 + \text{c.c.}, \quad (19)$$

$$\mathcal{H}_Q{}^1 \equiv 2\sum_{i \neq j} Q_{ij}\{i^{+z}[j^{zz} - j^{00}(1 - \gamma_{ij}{}^2)]$$
$$+ i^{++}j^{-z}(1 - \gamma_{ij}{}^2)\}m_{ij}\gamma_{ij} + \text{c.c.},$$

$$\mathcal{H}_Q{}^0 \equiv \sum_{i \neq j} Q_{ij}\{i^{++}j^{--}(1 - \gamma_{ij}{}^2)^2 + 4i^{+z}j^{-z}\gamma_{ij}{}^2(1 - \gamma_{ij}{}^2)$$
$$+ \tfrac{1}{2}[i^{zz} - i^{00}(1 - \gamma_{ij}{}^2)][j^{zz} - j^{00}(1 - \gamma_{ij}{}^2)]\}.$$

Before proceeding to the evaluation of the anisotropy constants, it is worth mentioning that $\mathcal{H}_D$ is zero in the ground state of a cubic crystal. In other words, the energy of a classical array of aligned dipoles is independent of the direction of alignment. The energy of a classical array of parallel quadrupoles, however, does depend on the direction of alignment. Note that $\mathcal{H}_Q$ has meaning only if $S \geq 1$. The major contributions to K_1 are from $\mathcal{H}_Q$ in first order and $\mathcal{H}_D$ in second order. The largest contributions to K_2 are from $\mathcal{H}_Q$ and $\mathcal{H}_D\mathcal{H}_Q$ in second order and from $\mathcal{H}_D$ in third order. These last three terms, of course, also make small contributions to K_1. First-order terms are essentially classical in nature and correspond to the long-wavelength limit of

[15] B. R. Cooper and F. Keffer, Phys. Rev. 125, 896 (1962).

spin-wave theory. Higher order perturbation terms are quantum effects and correspond to the contributions of (virtual) spin waves of large $\mathbf{k}$. The coupling constants J_{ij}, D_{ij}, and Q_{ij} are considered to be independent of temperature and of very short range; they are taken as J, D, and Q for nearest neighbors and zero otherwise. The pseudodipolar coupling will be understood to include the effect of the magnetic dipole interaction. Although this latter interaction is proportional to $r_{ij}{}^{-3}$, it is relatively small and falls off sufficiently fast when squared to be included with the very short range D.

III. THE ANISOTROPY CONSTANT $K_1(0)$

A. Van Vleck's Result

The principal contributions to K_1 at $0°\text{K}$ are

$$K_1(0) = K_{1D}(0) + K_{1Q}(0), \quad (20)$$

where

$$K_{1D}(0) = -(9/8)NS^2(D^2/2g\mu_B H_E)\Omega_{14}, \quad (21)$$

$$K_{1Q}(0) = \tfrac{1}{2}N(S - \tfrac{1}{2})^2 S^2 Q\Omega_{14}. \quad (22)$$

Here Ω_{14} is the lattice sum,

$$\Omega_{14} \equiv (10/3)\sum_h(\bar{\alpha}_h{}^2\bar{\beta}_h{}^2 + \bar{\alpha}_h{}^2\bar{\gamma}_h{}^2 + \bar{\beta}_h{}^2\bar{\gamma}_h{}^2 - \tfrac{1}{5}), \quad (23)$$

with $\bar{\alpha}_h$, $\bar{\beta}_h$, $\bar{\gamma}_h$ being the direction cosines of the nearest neighbor vector, $\mathbf{r}_h$, relative to the cubic axes. The values of Ω_{14} are

$$\Omega_{14} = -4, \; 32/9, \; 2, \quad (24)$$

for simple cube, body-centered cube, and face-centered cube, respectively; the subscripts indicate that Ω_{np} represents the contribution of $\sum_h \gamma_h{}^p$ to the anisotropy constant K_n. This notation differs slightly from that of Van Vleck and later authors, but is more convenient when the calculations are carried to higher order.

It was noted by Van Vleck that K_{1D} is intrinsically negative for bcc and fcc crystals, while K_{1Q} takes the sign of Q. In iron, since K_1 is positive, K_{1Q} must be positive and greater than $|K_{1D}|$. No further knowledge of the relative size or sign of D and Q is available from this one equation, but as Nagamiya[16] has suggested, evaluation of K_2 in terms of D and Q will provide a second equation to be solved in conjunction with Eq. (20).

A spin wave analysis[4] corrects K_{1D} so that Eq. (21) becomes

$$K_{1D}(0) = -(9/8)\eta(1 + 0.222\Delta)NS^2$$
$$\times[D^2/2J(2SZ - \eta)]\Omega_{14}, \quad (25)$$

where

$$\eta = 1.111, \; 1.071, \; 0.9793, \quad (26)$$

and

$$\Delta = 0, \; 0, \; 1, \quad (27)$$

for sc, bcc, and fcc, respectively.[17] The energy denominator in Eq. (25) may be interpreted in the following

[16] T. Nagamiya (private communication to F. Keffer).

[17] The coefficient of Δ in Eq. (25) and the values of η in Eq. (26) are corrected values of the corresponding quantities in references 4 and 15.

manner. First, the molecular field energy denominator, $2g\mu_B H_E$ as in Eq. (21), is replaced by the equivalent spin wave value, $4JSZ$ (constant denominator approximation). This is the energy required to reverse two noninteracting spins. Next, allowing for the exchange interaction of spin waves, one sees that while the energy needed to reverse the first spin is $2JSZ$, the energy to reverse the second spin (on a different atom) in the presence of the first is, on the average, only $2J(SZ-1)$. The energy denominator is the sum of these two partial energies, or $2J(2SZ-1)$. Finally, the η correction in Eq. (25) is the result of performing a numerical integration in $\mathbf{k}$ space while allowing the energy denominator to be a function of $\mathbf{k}$ (in the constant denominator or molecular field approximation $\eta=1$). The Δ correction indicates that there are additional terms in the fcc case only, since two nearest neighbors of a given atom may also be mutually nearest neighbors.

B. Higher Order Terms

The following additional terms in $K_1(0)$ are the byproduct of the higher order calculations required for $K_2(0)$; they are at least an order of magnitude smaller than the terms considered in the previous section. The energy denominators have been corrected to include the effect of spin wave interactions in the constant denominator approximation. The higher order terms are

$$K_{1DQ}'(0)=3N(S-\tfrac{1}{2})^2 S^2[DQ/2J(2SZ-1)]$$
$$\times(\Omega_{16}-2\Omega_{14}), \quad (28)$$

$$K_{1Q}'(0)=-2N(S-\tfrac{1}{2})^4 S^2[Q^2/2J(2SZ-1)]$$
$$\times(\Omega_{18}-2\Omega_{16}+\Omega_{14})$$
$$+N(S-\tfrac{1}{2})^3 S^2[Q^2/2J(3SZ-2)]$$
$$\times(\Omega_{18}-3\Omega_{16}+3\Omega_{14})$$
$$-\tfrac{1}{8}N(S-\tfrac{1}{2})^2 S^2[Q^2/8J(SZ-1)]$$
$$\times(\Omega_{18}-4\Omega_{16}+6\Omega_{14}), \quad (29)$$

$$K_{1D}'(0)=-(9/8)NS^2\{D^3/[2J(2SZ-1)]^2\}$$
$$\times(3\Omega_{16}-7\Omega_{14}-42S\Delta), \quad (30)$$

where Ω_{14} and Δ are the same as previously defined, and

$$\Omega_{16}\equiv(21/2)\sum_h[\bar{\alpha}_h^2\bar{\beta}_h^2\bar{\gamma}_h^2-(11/21)(\bar{\alpha}_h^2\bar{\beta}_h^2$$
$$+\bar{\alpha}_h^2\bar{\gamma}_h^2+\bar{\beta}_h^2\bar{\gamma}_h^2)+2/21], \quad (31)$$

$$\Omega_{18}\equiv-12\sum_h[\bar{\alpha}_h^4\bar{\beta}_h^4+\bar{\alpha}_h^4\bar{\gamma}_h^4+\bar{\beta}_h^4\bar{\gamma}_h^4)$$
$$+(17/6)\bar{\alpha}_h^2\bar{\beta}_h^2\bar{\gamma}_h^2-(5/6)(\bar{\alpha}_h^2\bar{\beta}_h^2+\bar{\alpha}_h^2\bar{\gamma}_h^2$$
$$+\bar{\beta}_h^2\bar{\gamma}_h^2)+1/9]. \quad (32)$$

Note that the Δ correction does not appear in second-order terms when the constant denominator approximation is used. The values of all Ω_{np} for sc, bcc, and fcc are given in Table I.

IV. THE ANISOTROPY CONSTANT $K_2(0)$

The second anisotropy constant in cubic, ferromagnetic crystals is found to have the following value at 0°K:

$$K_2(0)=K_{2DQ}(0)+K_{2Q}(0)+K_{2D}(0), \quad (33)$$

TABLE I. Values of the lattice sums Ω_{np} in cubic crystals.

Ω_{np}	sc	bcc	fcc
Ω_{14}	-4	32/9	2
Ω_{16}	-6	32/9	9/2
Ω_{18}	-8	64/27	5
Ω_{26}	6	128/9	$-39/2$
Ω_{28}	16	256/9	-31
Ω_{38}	4	128/81	9/2

where

$$K_{2DQ}(0)=3N(S-\tfrac{1}{2})^2 S^2[DQ/2J(2SZ-1)]\Omega_{26}, \quad (34)$$

$$K_{2Q}(0)=-2N(S-\tfrac{1}{2})^4 S^2[Q^2/2J(2SZ-1)](\Omega_{28}-2\Omega_{26})$$
$$+N(S-\tfrac{1}{2})^3 S^2[Q^2/2J(3SZ-2)](\Omega_{28}-3\Omega_{26})$$
$$-\tfrac{1}{8}N(S-\tfrac{1}{2})^2 S^2[Q^2/8J(SZ-1)]$$
$$\times(\Omega_{28}-4\Omega_{26}), \quad (35)$$

$$K_{2D}(0)=-(27/8)NS^2\{D^3/[2J(2SZ-1)]^2\}$$
$$\times(\Omega_{26}+54S\Delta). \quad (36)$$

Here again Δ denotes the fcc only terms, and

$$\Omega_{26}\equiv(231/2)\sum_h[\bar{\alpha}_h^2\bar{\beta}_h^2\bar{\gamma}_h^2-(1/11)(\bar{\alpha}_h^2\bar{\beta}_h^2$$
$$+\bar{\alpha}_h^2\bar{\gamma}_h^2+\bar{\beta}_h^2\bar{\gamma}_h^2)+2/231], \quad (37)$$

$$\Omega_{28}\equiv52\sum_h[(\bar{\alpha}_h^4\bar{\beta}_h^4+\bar{\alpha}_h^4\bar{\gamma}_h^4+\bar{\beta}_h^4\bar{\gamma}_h^4)$$
$$+(139/26)\bar{\alpha}_h^2\bar{\beta}_h^2\bar{\gamma}_h^2-(17/26)(\bar{\alpha}_h^2\bar{\beta}_h^2$$
$$+\bar{\alpha}_h^2\bar{\gamma}_h^2+\bar{\beta}_h^2\bar{\gamma}_h^2)+2/39]; \quad (38)$$

the numerical values of Ω_{26} and Ω_{28} are given in Table I. All contributions to $K_2(0)$ arising in second order perturbation are included in (34) and (35). Equation (36) is third order and is expected to be at least an order of magnitude larger than the other third-order terms such as $\mathcal{K}_D\mathcal{K}_D\mathcal{K}_Q$ which have been neglected. The only useful comment on the sign of $K_2(0)$ is that, for $S=\tfrac{1}{2}$, $K_2(0)=K_{2D}(0)$ which is positive (negative) when D is negative (positive).

V. THE COUPLING CONSTANTS D AND Q

Since there are now two equations relating the pseudodipolar and pseudoquadrupolar coupling constants to the anisotropy constants and exchange integral, it should be possible to infer the values of D and Q using measured values of K_1, K_2, and J. While this is true in principle, it is not always so in practice. The anisotropy constants, particularly K_2, are very difficult to determine experimentally, not only in magnitude, but also in sign. For nickel, for example, there are reported values of K_2 which are roughly equal in magnitude but opposite in sign. A further complication in the case of nickel, which effectively has a magnetic moment of $0.6\mu_B$ per atom, is that the calculational model is based on an integral number of spins per atom. This latter condition is better suited to iron with $2.2\mu_B$ per atom or to cobalt with $1.7\mu_B$ per atom. To minimize the error in assuming $S=\tfrac{1}{2}$ for Ni and $S=1$ for Fe and Co, the product JS is used wherever

TABLE II. Coupling constants $(D/J, Q/J)$ for Fe using $K_1(0) = 5.23 \times 10^5$ ergs/cm³.

$K_2(0)$ $(10^5$ ergs/cm³) \ JS $(10^{-14}$ erg)	3.60	2.87	1.88
1.5	0.0877, 0.00171	0.0939, 0.00200	0.106, 0.00269
1.0	0.0743, 0.00134	0.0793, 0.00157	0.0893, 0.00212
0.5	0.0544, 0.000896	0.0577, 0.00106	0.0640, 0.00145

possible in the K_1 and K_2 equations. This product, rather than J or S alone, is determined by spin wave resonance experiments and measurement of the $T^{3/2}$ coefficient of the spontaneous magnetization. In like manner an S is affixed to D and Q.

A. Iron: bcc, $S = 1$

Sato and Chandrasekhar[18] have made a very careful measurement of the second anisotropy constant of Fe. They found $K_2(300) = 0.714 \times 10^5$ ergs/cm³ and $K_2(77) = 0.904 \times 10^5$ ergs/cm³. Graham[9] has estimated that $K_2 = (0 \pm 0.50) \times 10^5$ ergs/cm³ at these temperatures. For the present calculations the value of $K_2(0)$ is taken to be 1.0×10^5 ergs/cm³. The value of $K_1(0)$ is 5.23×10^5 ergs/cm³.[9] A best value of JS is determined from the $T^{3/2}$ coefficient measured by Budnick et al.[19]: $JS = 2.87 \times 10^{-14}$ erg. Also considered are a maximum $JS = 3.60 \times 10^{-14}$ erg from the exchange constant measured by Rodbell[20] and a minimum $JS = 1.88 \times 10^{-14}$ erg from the mnemonic formula of Rushbrooke and Wood[21] using $T_c = 1043°K$ and $S = 1$.

The two polynomial equations in D and Q were solved for the ratios D/J and Q/J (more precisely DS/JS and QS/JS) using the numerical coefficients appropriate to bcc and $S = 1$. The best values are $D/J = 0.0793$, $DS = 2.28 \times 10^{-15}$ erg, and $Q/J = 0.00157$, $QS = 4.50 \times 10^{-17}$ erg. The ratio of D to the purely magnetic dipole coupling constant for nearest neighbors in Fe is about 93. Values corresponding to extremes of JS and $K_2(0)$ are given in Table II. Both D and Q are positive. Even substitution of $K_2(0) = 0$ in the equations yields small, but positive, coupling constants.

When the quadrupole interaction exists, i.e., when $S \geq 1$ as in the case of iron, the lowest order contribution to the third anisotropy constant, K_3, arises from $\mathcal{H}_Q$ in second-order perturbation and is probably representative of the magnitude of K_3. In this case

$$K_{3Q}(0) = -N(S-\tfrac{1}{2})^2 S^2 (Q^2/2J)[2(S-\tfrac{1}{2})^2/(2SZ-1)$$
$$- (S-\tfrac{1}{2})/(3SZ-2) + 1/32(SZ-1)]\Omega_{38}, \quad (39)$$

where

$$\Omega_{38} \equiv (130/3) \sum_h [(\bar{\alpha}_h{}^4 \bar{\beta}_h{}^4 + \bar{\alpha}_h{}^4 \bar{\gamma}_h{}^4 + \bar{\beta}_h{}^4 \bar{\gamma}_h{}^4)$$
$$+ (6/5)\bar{\alpha}_h{}^2 \bar{\beta}_h{}^2 \bar{\gamma}_h{}^2 - (18/65)(\bar{\alpha}_h{}^2 \bar{\beta}_h{}^2$$
$$+ \bar{\alpha}_h{}^2 \bar{\gamma}_h{}^2 + \bar{\beta}_h{}^2 \bar{\gamma}_h{}^2) + 1/65]. \quad (40)$$

[18] H. Sato and B. S. Chandrasekhar, J. Phys. Chem. Solids 1, 228 (1957).
[19] J. I. Budnick, L. J. Bruner, R. J. Blume, and E. L. Boyd, Suppl. J. Appl. Phys. 32, 120 (1961).
[20] D. S. Rodbell, in Growth and Perfection in Crystals (John Wiley & Sons, Inc., New York, 1958), p. 247.
[21] G. S. Rushbrooke and P. J. Wood, Mol. Phys. 1, 257 (1958).

Values of Ω_{38} for the three lattices are given in Table I. The third anisotropy constant is the coefficient of $(\alpha_1{}^4 \alpha_2{}^4 + \alpha_1{}^4 \alpha_3{}^4 + \alpha_2{}^4 \alpha_3{}^4)$ in the anisotropic free energy, Eq. (1). Using $QS = 4.50 \times 10^{-17}$ erg and $JS = 2.87 \times 10^{-14}$ erg, the predicted value of $K_{3Q}(0)$ for Fe is -18 ergs/cm³, about four orders of magnitude smaller than $K_2(0)$.

In reference 15 Cooper and Keffer have related the unusually large paramagnetic resonance linewidths in ferromagnets to the theoretical coupling constants J, D, and Q, and thereby to the measured anisotropy constant, K_1. Presuming these constants to be temperature insensitive, the relation between linewidth and anisotropy is

$$\Delta H \approx f(S,s)[K_1(0)/N]\epsilon, \quad (41)$$

where $f(S,s)$ is a function of atomic spin and crystal structure, and

$$\epsilon \equiv |K_{1D}(0)|/K_1(0). \quad (42)$$

The pseudoquadrupolar portion of the anisotropy makes a negligible contribution to the linewidth. For iron, taking the value of $f(S,s)$ from Cooper and Keffer, we find $\Delta H \sim 1.1 \times 10^4 \epsilon$ Oe. The value of ϵ from the present paper is 4.6, while Buslik[22] has calculated the dependence of the linewidth on temperature in the neighborhood of the Curie point and deduces a value of $\epsilon \approx 2.5$. The predicted linewidth is thus of the order of 40 kOe for iron.

B. Cobalt: fcc, $S = 1$

Using ferromagnetic resonance techniques Rodbell[18] recently measured the equivalent anisotropy fields, K/M, of cobalt stabilized in the face-centered cubic structure. From his data at 4.2°K the derived values of the anisotropy constants are $K_1(0) = -9.0 \times 10^5$ ergs/cm³ and $K_2(0) = -2.0 \times 10^5$ ergs/cm³. In contrast with iron and nickel, the temperature dependence of K_1 for cobalt apparently follows the 10th power law quite well with only a slight modification for thermal expansion. In the case of a thin film sample, $K_2(T)$ anomalously followed a 10th power law, but $K_2(T)$ of a second sample consisting of precipitate particles followed the theoretical 21st power law. The temperature dependence was determined by comparison with Jaccarino's measurements[23] of the nuclear magnetic resonance frequency which is proportional to the magnetization. From the coefficient of the $T^{3/2}$ term in

[22] A. J. Buslik, thesis, University of Pittsburgh, 1962 (unpublished).
[23] V. Jaccarino, Bull. Am. Phys. Soc. 4, 461 (1959).

TABLE III. Coupling constants $(D/J, Q/J)$ for Co using $K_1(0) = -9.0 \times 10^5$ ergs/cm^3.

$K_2(0)$ $(10^5$ ergs/cm$^3)$ \ JS $(10^{-14}$ erg)	3.0	2.0	1.6
−3.0	0.107, 0.00125	0.125, 0.00148	0.136, 0.00160
−2.0	0.0969, 0.000780	0.113, 0.000865	0.124, 0.000897
−1.0	0.0828, 0.000219	0.0976, 0.000143	0.107, 0.0000645

the magnetization expression fit to Jaccarino's data the product $JS = 2.0 \times 10^{-14}$ erg is deduced.

The atomic coupling constants were determined in the same manner as for iron. Both D and Q are positive over a wide range of values of K_1, K_2, and JS, with no indication of a change of sign. Rodbell's value of $K_1(0)$ was adopted as standard while his $K_2(0)$ was varied by $\pm 50\%$. The value of JS from Jaccarino's experiment was taken as a best value with extremes of 3.0×10^{-14} and 1.6×10^{-14} erg also being considered. The latter number was calculated from the Rushbrooke and Wood formula using $T_c = 1394°$K and $S = 1$.

The best values of the Co coupling constants are $D/J = 0.113$, $DS = 2.26 \times 10^{-15}$ erg, and $Q/J = 0.000865$, $QS = 1.73 \times 10^{-17}$ erg. The ratio of D to the purely magnetic dipole coupling constant for nearest neighbors in cobalt is about 98. Additional values of D and Q are given in Table III. Substituting best values in Eq. (39), the predicted third anisotropy constant is $K_{3Q}(0) = -7.5$ ergs/cm^3, which is small enough relative to K_1 and K_2 to be ignored in practice. The value of ϵ for Co is 1.4, so that the paramagnetic linewidth is predicted to be about 80 kOe.

C. Nickel: fcc, $S = \frac{1}{2}$

The quadrupolar terms in the equations for K_1 and K_2 are identically zero when the spin is set equal to one-half. Although $S = \frac{1}{2}$ is not a good assumption for Ni, the calculational model insists on an integral number of spins per atom. Furthermore, Van Vleck[24] has estimated that the nickel atom, basically a mixture of $3d^9$ and $3d^{10}$ electronic states, spends less than 10% of its time in the $3d^8$ configuration which would provide an intrinsic quadrupole moment. The quadrupole-quadrupole interaction in nickel would, thus, be less than 1% of that in an atom which is normally in an $S = 1$ state. The possibility of a dipole-quadrupole interaction, i.e., an interaction linear in one spin and quadratic in another, is eliminated by the condition of time reversal invariance. Consequently, there is little choice in this model but to accept the K_1 and K_2 equations without the quadrupole terms. These equations are

$$K_1(0) = -(9/8)NS^2(D^2/2J)[\eta(1+0.222\Delta)\Omega_{14}/$$
$$(2SZ-\eta)+D(3\Omega_{16}-7\Omega_{14}-42S\Delta)/$$
$$2J(2SZ-1)^2], \quad (43)$$

[24] J. H. Van Vleck, Rev. Mod. Phys. 25, 220 (1953).

$$K_2(0) = -(27/8)NS^2D^3(\Omega_{26}+54S\Delta)/$$
$$[2J(2SZ-1)]^2, \quad (44)$$

where the values of η and Δ are given in Eqs. (26) and (27), respectively, and the values of Ω_{np} in Table I. Obviously, D is overdetermined and, as will be shown, the two equations are inconsistent.

The experimental values of K_1 for Ni are $K_1(77) = -6.4 \times 10^5$ ergs/cm^3 and $K_1(20) = -7.5 \times 10^5$ ergs/cm^3 as given by Bozorth,[25] and $K_1(77) = -5.4 \times 10^5$ ergs/cm^3 and $K_1(4.2) = -8.3 \times 10^5$ ergs/cm^3 as measured by Reich.[26] The extrapolated value of $K_1(0)$ is taken to be $K_1(0) = -8.5 \times 10^5$ ergs/cm^3. Reich also found $K_2(4.2) = (1.4 \pm 0.5) \times 10^5$ ergs/cm^3. However, Sato and Chandrasekhar[18] have pointed out that experimental measurements in the (110) plane, as were Reich's, would compound a 10% error in K_1 into a 100% error in K_2. Sato and Chandrasekhar determined K_2 from torque measurements in the (111) plane, the corresponding torque equation being independent of K_1. Their results are $K_2(300) = 0.234 \times 10^5$ ergs/cm^3 and $K_2(77) = 3.17 \times 10^5$ ergs/cm^3, both positive in sign. The value of K_2 at 0°K is assumed to be $K_2(0) = 4.0 \times 10^5$ ergs/cm^3.

The temperature dependence of the spontaneous magnetization of Ni has been measured by Pugh and Argyle.[27] Values of JS from their $T^{3/2}$ coefficient are $JS = 2.82 \times 10^{-14}$ erg (first report) and $(2.16 - 2.66) \times 10^{-14}$ erg (second report), the last two values being essentially the average values for two methods of analysis. Spin wave resonance experiments of Nosé[28] yield $JS = 2.5 \times 10^{-14}$ erg which is adopted here as a best value since it falls midway between the extremes of Pugh and Argyle. The Rushbrooke and Wood mnemonic formula gives a minimum $JS = 1.05 \times 10^{-14}$ erg using $T_c = 631°$K and $S = \frac{1}{2}$.

A quick evaluation of Eq. (43) using the discussed physical parameters for Ni, $S = \frac{1}{2}$, and lattice sums appropriate to fcc indicates that D/J is of the order of 0.1 with sign undetermined. A similar appraisal of Eq. (44) indicates $D/J \sim 1$ with sign opposite to that of $K_2(0)$. It is believed that the D^2/J term will always be the leading term in an expression for K_1, so the sign of D is assumed to be opposite that of the experi-

[25] R. M. Bozorth, Ferromagnetism (D. Van Nostrand Company, Inc., New York, 1951), p. 569.
[26] K. H. Reich, Phys. Rev. 101, 1647 (1956).
[27] E. W. Pugh and B. E. Argyle, Suppl. J. Appl. Phys. 32, 334 (1961); J. Appl. Phys. 33, 1178 (1962).
[28] H. Nosé, J. Phys. Soc. Japan 16, 2475 (1961).

TABLE IV. Pseudodipolar coupling constant D/J and second anisotropy constant $K_2(0)$ (10^5 ergs/cm^3), for Ni.

$K_1(0)$ \ JS (10^5 ergs/cm^3) \ (10^{-14} erg)	2.82	2.50	1.05
-9.5	$-0.0766, 0.304$	$-0.0810, 0.319$	$-0.124, 0.482$
-8.5	$-0.0723, 0.256$	$-0.0768, 0.271$	$-0.117, 0.407$
-7.5	$-0.0680, 0.213$	$-0.0721, 0.225$	$-0.112, 0.354$

mental value of K_2, and then the magnitude of D is determined from Eq. (43). Finally, a value of $K_2(0)$ is calculated from Eq. (44).

The best value of D/J is -0.0768 and $DS=-1.92$ $\times 10^{-15}$ erg. This value of D is about 140 times larger than the nearest neighbor magnetic dipole coupling constant. The corresponding value of $K_2(0)$ is 0.271 $\times 10^5$ ergs/cm^3. Additional values of D and K_2 corresponding to extremes of JS and K_1 are given in Table IV. Although the calculated ratios of pseudodipolar to exchange coupling seem to be of the right size, the associated values of $K_2(0)$ are about a factor of 10 smaller than the experimental value. This discrepancy was also noted by Hurwitz.[29] (See further discussion in Sec. VI.) If $Q \equiv 0$ is presumed for Ni, the principal contribution to $K_3(0)$ arises in fourth-order perturbation and has not been calculated. The value of ϵ for nickel is unity and the paramagnetic linewidth as predicted by Cooper and Keffer is about 50 kOe.

VI. SUMMARY AND DISCUSSION

Van Vleck's molecular field theory of ferromagnetic anisotropy was extended to provide an evaluation of the second anisotropy constant in cubic crystals at the absolute zero of temperature. Corrections derived from spin wave theory were applied so that the third-order perturbation terms would be significant. Measured values of the anisotropy constants and the exchange integral were then used to calculate the magnitudes of the phenomenological pseudopolar coupling constants for cubic iron, cobalt, and nickel. The resulting D and Q appear satisfactory for Fe and Co, but not for Ni. In turn, these constants were used to predict the size of the third anisotropy constant and the value of the paramagnetic resonance linewidth.

There has been one previous calculation of K_2 using Van Vleck's theory. Hurwitz[29] evaluated the second anisotropy constant using only the pseudodipolar term

for application to nickel. He found that if the dipolar coupling, D, were chosen to match theoretical and experimental values of K_1, the theoretical K_2 would be an order of magnitude too small. Conversely, if the two values of K_2 were made to agree through choice of D, then the theoretical K_1 would be too large. This conclusion was corroborated by the present work (see Sec. VC) and the inconsistency is unlikely to be resolved without a new approach to the mechanism responsible for the anisotropy in nickel.

At the time of his work, Hurwitz did not consider the third-order corrections to K_1, which are incidental to the calculation of K_2, as being significant because the uncertainties in the basic, second-order, molecular field calculation were of the same order of magnitude. Now that the molecular field approximation has been assessed and corrected by spin wave theory,[4] the third-order terms become significant. As Hurwitz expected, however, they are small $[K_{1D}'(0) \approx 0.03 K_{1D}(0)$ in Ni$]$ and do not seriously affect any of the previous results. Hurwitz also concluded that the Van Vleck model could not predict the correct temperature dependence of the anisotropy, especially in nickel.

Since the present calculations were limited to 0°K, the inability of this model to describe the effect of temperature on the anisotropy, except perhaps in cobalt, was not of primary concern. This shortcoming, however, may be allied to another difficulty, namely, that the calculational model is based on an integral number of spins per atom. It, thus, inherently assumes, for example, that all the atoms in nickel are in a $3d^9$ electronic configuration, whereas, to a first approximation, only 60% are in this configuration and the rest in $3d^{10}$. An improved ground-state Hamiltonian which mixes the requisite amount of d^9 and d^{10} configurations might reasonably be expected to help reconcile the nickel calculations with the physical situation.

[29] H. Hurwitz, Jr., thesis, Harvard University, 1941 (unpublished).